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# First-Principles Microkinetic Model for Low-Temperature NH<sub>3</sub>-Assisted Selective Catalytic Reduction of NO over Cu-CHA

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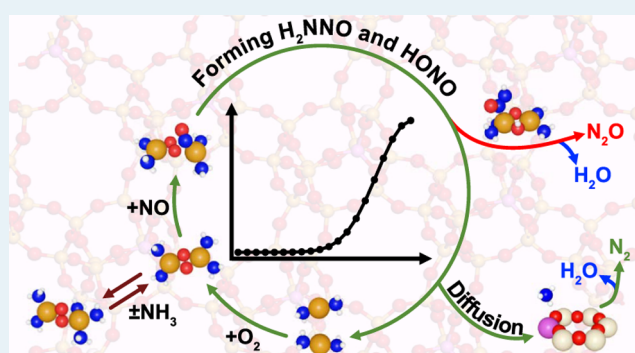
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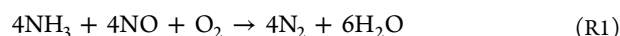
**ABSTRACT:** A first-principles microkinetic model is developed to investigate the low-temperature ammonia-assisted selective catalytic reduction (NH<sub>3</sub>-SCR) of NO over Cu-chabazite (Cu-CHA). The reaction proceeds over NH<sub>3</sub>-solvated Cu sites by the formation of H<sub>2</sub>NNO and HONO, which decompose to N<sub>2</sub> and H<sub>2</sub>O over Brønsted acid sites. Nonselective N<sub>2</sub>O formation is considered by H<sub>2</sub>NNO decomposition over the Cu sites. The adsorption of NH<sub>3</sub> at oxidized Cu sites is found to inhibit the reaction at low temperatures by hindering NO adsorption. For the reactions, we find positive reaction orders with respect to NO and O<sub>2</sub>, whereas the reaction order with respect to NH<sub>3</sub> is negative. The reaction orders and the obtained apparent activation energy are in good agreement with experimental data. A degree of rate control analysis shows that NH<sub>3</sub>-SCR over a pair of Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> is mainly controlled by NO adsorption below 200 °C, whereas the formation of HONO and H<sub>2</sub>NNO becomes controlling at higher temperatures. The successful formulation of a first-principles microkinetic model for NH<sub>3</sub>-SCR rationalizes previous phenomenological models and links the kinetic behavior with materials properties, which results in unprecedented insights into the function of Cu-CHA catalysts for NH<sub>3</sub>-SCR.

**KEYWORDS:** first-principles microkinetic modeling, Cu-CHA, NH<sub>3</sub>-SCR, N<sub>2</sub>O formation, entropy evaluation



## INTRODUCTION

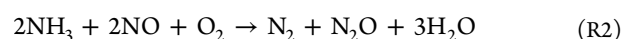
Combustion in oxygen excess is energy-efficient but requires catalytic aftertreatment systems to control NO<sub>x</sub> emissions.<sup>1</sup> The current technology for lean-burn NO<sub>x</sub> reduction is selective catalytic reduction (SCR) with ammonia as the reducing agent (NH<sub>3</sub>-SCR), which reduces NO<sub>x</sub> emissions efficiently.<sup>1</sup> Catalysts based on Cu-chabazite (Cu-CHA) are common catalysts for NH<sub>3</sub>-SCR thanks to the low-temperature activity and good hydrothermal stability.<sup>1–3</sup> The overall NH<sub>3</sub>-SCR reaction with only NO (standard SCR) is



This is a redox reaction that requires catalytic sites that can change oxidation state during the reaction, which for Cu means an alternation between Cu<sup>I</sup> and Cu<sup>II</sup>. The NH<sub>3</sub>-SCR reaction has been kinetically characterized by measurements of apparent activation energies and reaction orders. Under typical conditions for low-temperature NH<sub>3</sub>-SCR (150–250 °C), the apparent activation energy for NH<sub>3</sub>-SCR has been reported to be in the range of 0.4–0.8 eV.<sup>4–6</sup> The range in apparent activation energies can be ascribed to differences in Cu loading and presence of H<sub>2</sub>O. The reaction order for NO conversion with respect to O<sub>2</sub> has been measured to be between 0.2 and 0.5,<sup>4,7</sup> whereas the reaction order with respect to NO is 0.7–0.9.<sup>4,7</sup>

Furthermore, the reaction order with respect to NH<sub>3</sub> is zero or slightly negative when the NH<sub>3</sub>-to-NO<sub>x</sub> ratio is close to 1,<sup>4</sup> indicating that NH<sub>3</sub> inhibits the NH<sub>3</sub>-SCR reaction. The reaction order of NH<sub>3</sub> depends on the NH<sub>3</sub>-to-NO<sub>x</sub> ratio and has recently been measured to be positive at low (0.1–0.5) ratios.<sup>8</sup>

An unwanted side reaction during NH<sub>3</sub>-SCR is the partial reduction of NO to N<sub>2</sub>O, which is a potent greenhouse gas receiving increasing attention.<sup>9</sup> One proposed overall reaction for N<sub>2</sub>O formation is

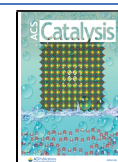


Different mechanistic reaction paths may exist for N<sub>2</sub>O formation, and NH<sub>4</sub>NO<sub>3</sub> has been discussed as an intermediate at high temperatures (above 250 °C).<sup>10–12</sup> However, N<sub>2</sub>O is formed also at lower temperatures over Cu-CHA and the N<sub>2</sub>O formation profile has been measured to follow that of NH<sub>3</sub>-

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SCR.<sup>6,13</sup> The apparent activation energy for low-temperature N<sub>2</sub>O formation has been measured to be 0.36 eV,<sup>14</sup> which is lower than the apparent activation energy for the NH<sub>3</sub>-SCR reaction.

In recent years, significant advances have been made in the understanding of the active sites and the reaction mechanism of low-temperature NH<sub>3</sub>-SCR reaction over Cu-CHA catalyst. The current understanding is based on in situ X-ray absorption spectroscopy experiments in combination with density functional theory (DFT) calculations. It is now established that the ion-exchanged Cu does not occupy fixed positions in the zeolite during low-temperature operation but forms instead mobile NH<sub>3</sub>-solvated complexes.<sup>15–20</sup>

The adsorption of O<sub>2</sub> is a key step in the reaction mechanism, which requires a pair of [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes, forming [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> species.<sup>17,21–24</sup> Activation of O<sub>2</sub> induces the change in oxidation state of Cu from Cu<sup>I</sup> to Cu<sup>II</sup> (and possibly Cu<sup>III</sup>),<sup>25,26</sup> which is known to be the active oxidation state for the subsequent NH<sub>3</sub>-assisted NO reduction.<sup>27</sup> Two atomistic reaction cycles for low-temperature NH<sub>3</sub>-SCR involving [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes and Brønsted acid sites were proposed recently based on density functional theory (DFT) calculation.<sup>18</sup> The activation of oxygen and the formation of the key intermediates HONO and H<sub>2</sub>NNO were suggested to occur over the Cu sites, whereas the Brønsted acid sites facilitate the subsequent decomposition of HONO and H<sub>2</sub>NNO to N<sub>2</sub> and H<sub>2</sub>O. The two proposed cycles differ in the way NO is adsorbed on the [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> complex; NO adsorbs either on the Cu cation, forming nitrosonium (NO<sup>+</sup>), or on an O atom forming a nitrite (NO<sub>2</sub><sup>−</sup>). The measured correlation between low-temperature N<sub>2</sub> and N<sub>2</sub>O formation suggests a reaction path where N<sub>2</sub>O formation is connected to the NH<sub>3</sub>-SCR reaction cycle. We have recently presented a DFT-based mechanism for H<sub>2</sub>NNO decomposition into N<sub>2</sub>O and H<sub>2</sub>O over a [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>OOH]<sup>2+</sup> complex.<sup>12</sup> The proposed reaction paths for N<sub>2</sub> and N<sub>2</sub>O formation have flat potential energy landscapes,<sup>12,18</sup> with the highest barriers related to the formation and decomposition of H<sub>2</sub>NNO. However, these reaction mechanisms have not been evaluated by microkinetic modeling and their kinetic behaviors are presently unknown.

Phenomenological kinetic models have previously been developed for the NH<sub>3</sub>-SCR reaction over Cu-CHA.<sup>14,28–31</sup> These models generally treat the SCR reaction, N<sub>2</sub>O formation, and NH<sub>3</sub> oxidation as global steps and consider schematic catalytic sites. For example, the model in ref 14 includes three catalytic sites, which are all associated with a combination of Cu and Brønsted acid sites. The formation of N<sub>2</sub>O is modeled with two reactions describing low- and high-temperature N<sub>2</sub>O formation, respectively.<sup>14</sup> The phenomenological models are based on experimental data and describe accurately steady-state and transient kinetic behavior. However, because of the lumped sites and reaction steps, the models do not provide clear links between materials properties and catalytic performance.

Herein, we develop a first-principles-based microkinetic model for NH<sub>3</sub>-SCR over Cu-CHA, which is based on an extension of the previously proposed atomistic mechanisms for N<sub>2</sub> and N<sub>2</sub>O formation.<sup>12,18</sup> DFT calculations are used to obtain the potential energy surfaces and the reaction kinetics is treated in the mean-field approximation. The potential energy surfaces are flat, and the reaction rate depends sensitively on changes in the entropy. Thus, the evaluation of entropy changes along the reaction path is given special attention. The results from the kinetic model are in good agreement with our kinetic

experiments of apparent activation energies, reaction orders, and N<sub>2</sub>O selectivity. The development of a successful first-principles-based microkinetic model for NH<sub>3</sub>-SCR over Cu-CHA demonstrates the capability of first-principles kinetic models, rationalizes previous phenomenological kinetic models, and forms the basis for further improvement of NH<sub>3</sub>-SCR catalysts.

## ■ COMPUTATIONAL AND EXPERIMENTAL METHODS

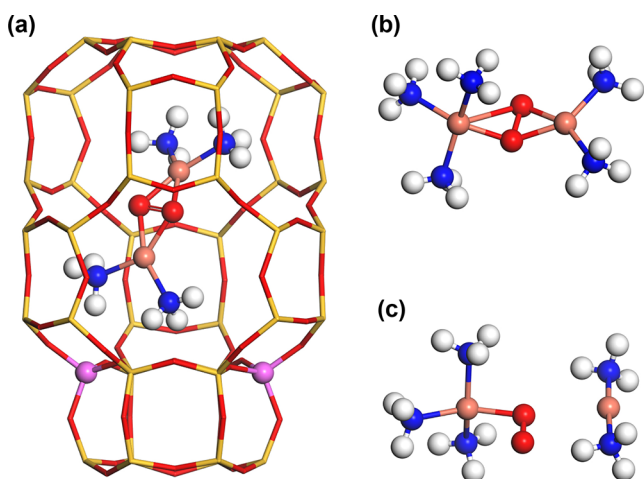
**First-Principles Calculation.** Spin-polarized density functional theory calculations are performed with the Vienna Ab initio Simulation Package (VASP).<sup>32–35</sup> The valence electrons are described with a plane-wave basis set using a cutoff energy of 480 eV, and the interaction between the valence and the core electrons is described with the projector augmented wave (PAW) method.<sup>36,37</sup> The number of valence electrons treated in the calculations are Cu(11), Si(4), Al(3), O(6), N(5), and H(1). The *k*-point sampling is restricted to the  $\Gamma$  point.

The gradient-corrected Perdew–Burke–Ernzerhof (PBE)<sup>38</sup> functional, augmented with a Hubbard-*U* term and van der Waals corrections, is used to describe exchange–correlation effects. A Hubbard-*U* term for Cu 3d is needed to properly describe enzymatic systems<sup>39,40</sup> with a similar Cu–OO–Cu core structure as the oxidized Cu species present during NH<sub>3</sub>-SCR over Cu-CHA. Here, we use a *U*-parameter of 6 eV for Cu 3d, which has been determined by comparisons with the crystal structure of Cu<sub>2</sub>O.<sup>39</sup> In addition, Grimme-D3 corrections have been applied to account for the van der Waals interactions of the molecules in the zeolites.<sup>41,42</sup>

For the structure optimization, the convergence criterion in the self-consistent field (SCF) loop is set to 1 × 10<sup>−5</sup> eV and the structures are considered to be relaxed when the force acting on each atom is less than 0.02 eV/Å. Transition-state structures and activation energies are calculated using the climbing image nudged elastic band (CI-NEB) method.<sup>43,44</sup> The transition-state structures are confirmed by vibrational analysis using the finite difference method. The search for low-energy structures is done by geometry-optimizing configurations obtained from Born–Oppenheimer ab initio molecular dynamics (AIMD) simulations, which are performed in the canonical (NVT) ensemble using a Nosé–Hoover thermostat.<sup>45,46</sup>

The chabazite structure is described in the rhombohedral unit cell, which contains 12 tetrahedral Si sites. The experimentally determined lattice parameters ( $\alpha = \beta = \gamma = 94.2^\circ$ ,  $a = b = c = 9.42$  Å) are used and fixed during the structural optimizations. To model Cu-exchanged CHA, two Si atoms in the six-membered ring of the zeolite cages are replaced by Al yielding a Si/Al ratio of 5. This ratio is similar to common experimental values<sup>6,19,47</sup> and, thus, is a reasonable choice when modeling the Cu-CHA material for NH<sub>3</sub>-SCR. A structural model of the chabazite cages, with a [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> complex and the considered Al distribution, is shown in Figure 1. The CHA framework consists of large cages consisting of four-, six-, and eight-membered rings and small cages with four- and six-membered rings.

**Microkinetic Modeling.** Mean-field microkinetic modeling is used to simulate the reaction kinetics. The numerical solution of the equilibrium reaction rate and coverages are obtained by solving a set of coupled ordinary differential equations, which describe the time evolution of the adsorbate coverages. The differential equation for adsorbate *i* is given by



**Figure 1.** (a) Side view of the chabazite cages showing the Al positions in the six-membered ring. The large cage includes the [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>)]<sup>2+</sup> complex. (b, c) Two structures of [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>3</sub>(O<sub>2</sub>)]<sup>2+</sup>. Atom color codes: Cu (bronze), Si (yellow), Al (pink), O (red), N (blue), and H (white).

$$\frac{d\theta_i}{dt} = \sum_j r_j(\vec{\theta})c_{ji} \quad (1)$$

where  $\theta_i$  is the fractional coverage of species  $i$  and  $r_j$  is the rate of reaction  $j$ , which depends on the fractional coverages ( $\vec{\theta}$ ). The number of  $i$  molecules consumed in reaction  $j$  is reflected in the stoichiometric number ( $c_{ji}$ ). The fractional coverage should in this case be understood as the fraction of Cu sites in the cycle being in a certain state. Thus, each state in the catalytic cycles represents a fractional coverage and the sum of all possible states is 1. The physical structure, composition, and action of the Cu sites change in a sequential manner along the reaction cycle, and DFT calculations show that the states are mutually exclusive. In the absence of reactants, the metal adsorption site corresponds to two [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes, whereas the Brønsted acid site corresponds to NH<sub>4</sub><sup>+</sup>. MATLAB is used with the ode23s solver to numerically integrate the system of differential equations until steady state is reached. The mean-field approach assumes a uniform sample with random distribution of reactants and intermediates. Thus, it is applicable in cases with Cu/Al ratios where Cu- and Brønsted acid sites are spatially connected. The model assumes that Cu-complex pairs form with high enough probability. The SCR rate has experimentally shown to scale linearly<sup>17</sup> with Cu loadings above 0.1 Cu/1000 Å<sup>3</sup>, and we anticipate that the model is valid for the Cu loadings in the linear regime.

The rate constants  $k^{\text{TST}}$  are computed according to the transition-state theory

$$k^{\text{TST}} = \frac{k_B T}{h} \frac{Z^\ddagger}{Z} \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $h$  is Planck's constant,  $Z$  is the partition function of the initial state, and  $Z^\ddagger$  is the partition function of the transition state without the reaction coordinate. In the transition state theory, the initial and transition states are assumed to be in equilibrium, which leads to the following expression for the rate constant<sup>48</sup>

$$\begin{aligned} k^{\text{TST}} &= \frac{k_B T}{h} e^{-\Delta G^\ddagger/k_B T} = \frac{k_B T}{h} e^{\Delta S^\ddagger/k_B} e^{-\Delta H^\ddagger/k_B T} \\ &\approx \frac{k_B T}{h} e^{\Delta S^\ddagger/k_B} e^{-\Delta E^\ddagger/k_B T} \end{aligned} \quad (3)$$

where  $\Delta G^\ddagger$  is the difference in Gibbs free energy between the initial and transition states, and  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$  are the corresponding differences in entropy and enthalpy, respectively. The  $pV$  dependence on enthalpy is neglected and, hence, the change enthalpy becomes equal to the change in energy ( $\Delta E^\ddagger$ ).

The reaction energy barriers for adsorption steps are zero except for O<sub>2</sub> adsorption, which has a low activation energy. All adsorption steps are, however, associated with entropy losses, which give rise to free energy barriers indicating that the rate constants are largely determined by entropy effects.

**Evaluation of Entropy Changes.** Because entropy effects contribute significantly to the values for the rate constants, special care is taken when evaluating the changes in entropy. The entropies for gas-phase molecules are, as usual, calculated via their vibrational, rotational, and translational partition functions, yielding

$$S^{\text{gas}} = S_{\text{vib}}^{\text{gas}} + S_{\text{rot}}^{\text{gas}} + S_{\text{trans}}^{\text{gas}} \quad (4)$$

Here,  $S_{\text{vib}}^{\text{gas}}$ ,  $S_{\text{rot}}^{\text{gas}}$ , and  $S_{\text{trans}}^{\text{gas}}$  are the vibrational, rotational, and translational entropies, respectively. It is generally challenging to describe changes in entropy during reactions in zeolites.<sup>49,50</sup> For NH<sub>3</sub>-SCR in Cu-CHA, the challenge arises because some species are weakly bound and because the entropy of the adsorption site, i.e., [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes, is lost upon O<sub>2</sub> adsorption. Because of the different nature of the reactions along the reaction path, different approaches are required to describe the entropy changes.

In most cases, the harmonic approximation is used to evaluate the entropies of adsorbed species and transition states. However, in cases where the reactant enters the zeolite from the gas phase and is not chemically bound to the Cu complex, the translational and rotational entropies are estimated to be 2/3 of the gas-phase values

$$S^{\text{zeo}} = S_{\text{vib}}^{\text{zeo}} + \frac{2}{3} \times (S_{\text{rot}}^{\text{gas}} + S_{\text{trans}}^{\text{gas}}) \quad (5)$$

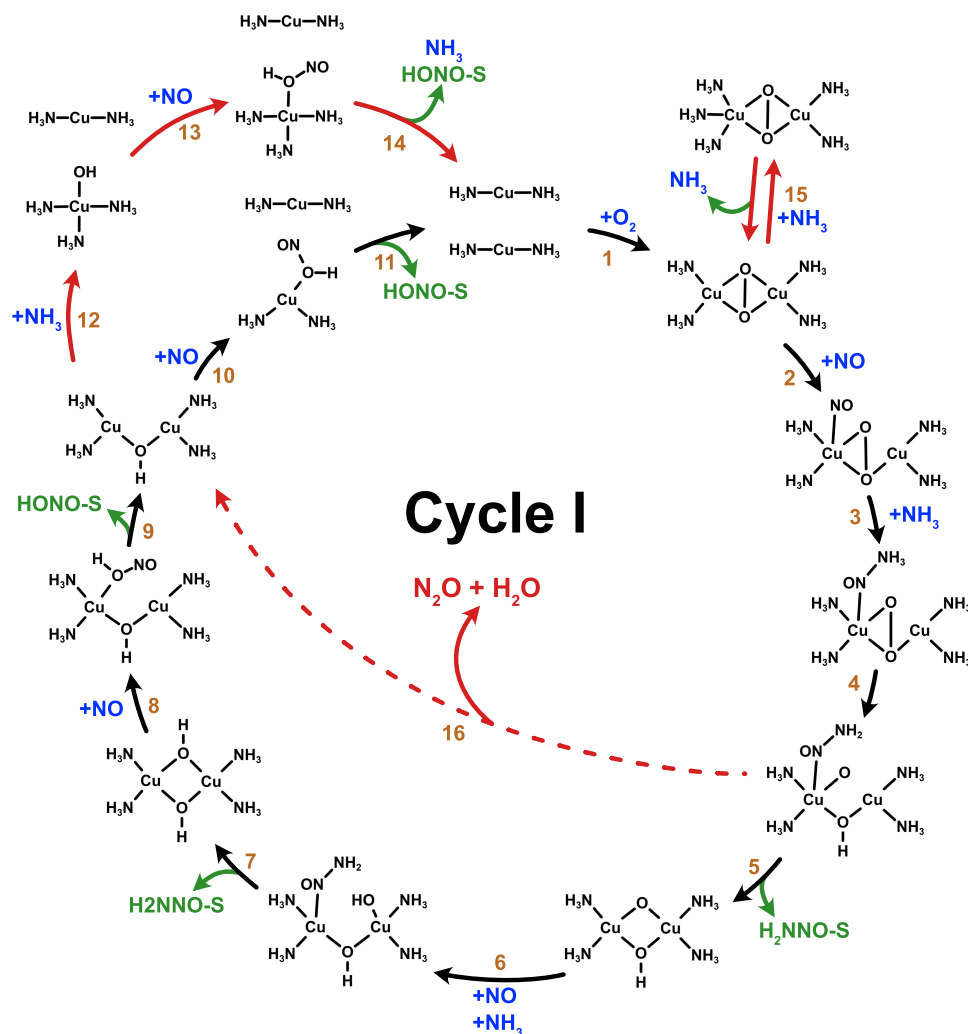
where  $S_{\text{vib}}^{\text{zeo}}$  is the vibrational entropy calculated in the zeolite. This approach yields reasonable values for nonbound small molecules, such as N<sub>2</sub> in zeolites.<sup>18,50</sup>

The entropy change upon O<sub>2</sub> adsorption forming the [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> complex is a special case as both O<sub>2</sub> and the [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes lose entropy during the reaction. The entropies of [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup>, and the transition state for O<sub>2</sub> adsorption are calculated by scaling the values of the gas-phase complexes according to

$$S^{\text{zeo}} = S_{\text{vib}}^{\text{zeo}} + 0.29 \times (S_{\text{rot}}^{\text{gas}} + S_{\text{trans}}^{\text{gas}}) \quad (6)$$

Here, the scaling of the rotational and translational entropies is reduced to 0.29 compared to the case with small molecules eq 5. The decreased scaling is motivated by the larger sizes of the complexes, which hinders the rotational and translational motions, resulting in an additional reduction of the entropy. The value of 0.29 has been determined by fitting temperature-programmed desorption (TPD) profiles of NH<sub>3</sub> from [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> in Cu-CHA (see the Supporting Information (SI)). Using the scaling of [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> also for the [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup>





**Figure 2.** Proposed reaction cycle I for low-temperature  $\text{NH}_3$ -SCR over Cu-CHA.

complex, the entropy differences of  $\text{O}_2$  adsorption in the forward reaction ( $\Delta S_{\text{f}}^{\text{zeo}}$ ) and backward reaction ( $\Delta S_{\text{b}}^{\text{zeo}}$ ) are evaluated as

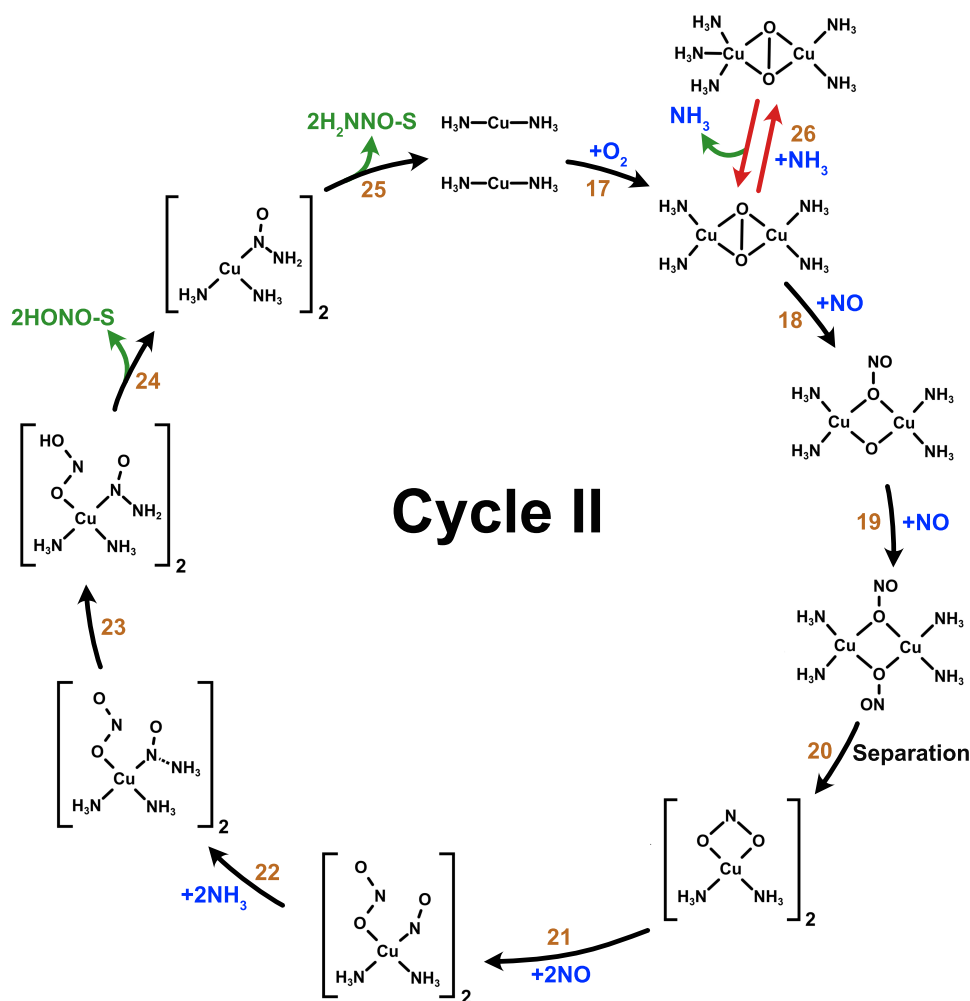
$$\Delta S_{\text{f}}^{\text{zeo}} = S_{\text{TS}[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}}^{\text{zeo}} - (2S_{[\text{Cu}(\text{NH}_3)_2]^+}^{\text{zeo}} + S_{\text{O}_2}^{\text{gas}}) \quad (7)$$

$$\Delta S_{\text{b}}^{\text{zeo}} = S_{\text{TS}[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}}^{\text{zeo}} - S_{[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}}^{\text{zeo}} \quad (8)$$

where  $S_{\text{TS}[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}}^{\text{zeo}}$  and  $S_{[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}}^{\text{zeo}}$  are the entropies of the transition- and final-state configurations, respectively.  $S_{[\text{Cu}(\text{NH}_3)_2]^+}^{\text{zeo}}$  is the entropy of the  $[\text{Cu}(\text{NH}_3)_2]^+$  complex in the zeolite. The experimentally determined value of the entropy loss for  $\text{O}_2$  adsorption on a pair of  $[\text{Cu}(\text{NH}_3)_2]^+$  complexes was recently reported to be  $142 \text{ J}/(\text{mol} \cdot \text{K})$ ,<sup>24</sup> which is close to our computational estimate of  $152 \text{ J}/(\text{mol} \cdot \text{K})$ . The good agreement between computed and measured entropy changes further validates the gas-phase scaling in eq 6.

**Experimental Methods. Sample Preparation.** The Cu-CHA catalysts were prepared from the same parent H-CHA material (Si/Al ratio 6.7), via impregnation with an aqueous solution of Cu nitrate. The Cu content in the Cu-CHA catalysts was varied to 1.6 and 3.2 wt % by an adjustment of the Cu nitrate concentration in the impregnation liquid. The impregnated catalysts were dried at  $100^\circ\text{C}$  and calcined in air at  $500^\circ\text{C}$  for 2 h.

**Kinetic Measurements.** The reaction order measurements are carried out in a flow reactor with 1.6 wt % Cu-CHA. The experimental setup consists of a gas mixing system, which includes mass flow controllers (Bronkhorst Hi-Tech), a powder reactor (Setaram Sensys DSC) with a vertically mounted quartz tube (inner diameter 4 mm), and a mass spectrometer (Airsense Compact, V&F). Cu-CHA sample (11.3 mg, 1.6 wt %) (sieve fraction  $300\text{--}355 \mu\text{m}$ ) is placed on a sintered quartz bed in the quartz tube. The total gas flow is  $300 \text{ NmL}/\text{min}$ , and the reaction temperature is  $200^\circ\text{C}$ . The sample is pretreated in  $\text{O}_2$  at  $500^\circ\text{C}$  for 30 min prior to the kinetic measurements. For the reaction order measurements with respect to NO, the concentrations of  $\text{NH}_3$  and  $\text{O}_2$  are held constant at 843 ppm and 10.3%, respectively. The NO concentration is varied from 88 to 722 ppm. In the measurement for the reaction order with respect to  $\text{NH}_3$ , the NO concentration and  $\text{O}_2$  concentrations are 109 ppm and 10.3%, respectively, and the  $\text{NH}_3$  concentration is varied between 190 and 1009 ppm. Finally, the concentration of  $\text{O}_2$  is varied from 1.1 to 10.3% in a mixture of 381 ppm NO and 641 ppm  $\text{NH}_3$ , to measure the reaction order with respect to  $\text{O}_2$ . The reaction conditions are maintained for at least 20 min for each concentration, allowing the reaction to reach steady state. Ar is used as balance in all measurements.



**Figure 3.** Proposed reaction cycle II for low-temperature  $\text{NH}_3$ -SCR over Cu-CHA.

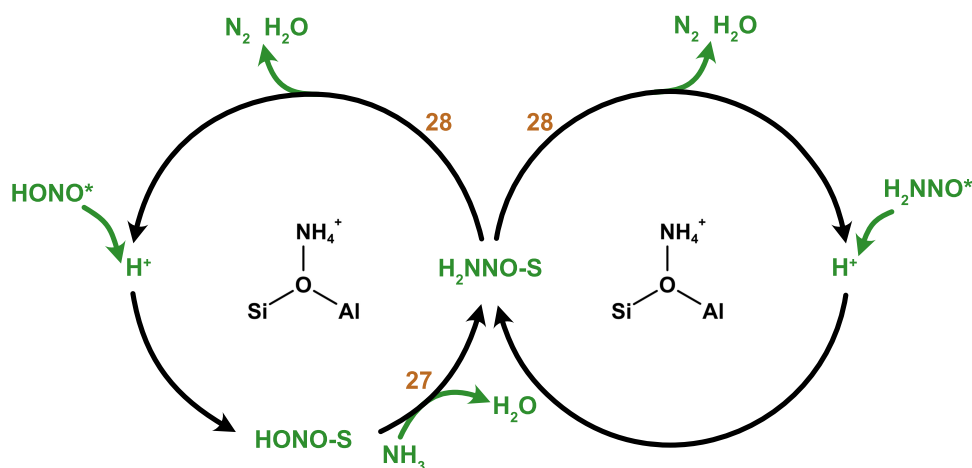
The conversion profiles for  $\text{NO}_x$  conversion are measured in a different powder reactor setup, using 10 mg of catalyst sample in a quartz U-tube reactor (inner diameter 4 mm, sieve fraction 150–300  $\mu\text{m}$ ), using a feed gas consisting of 500 ppm NO, 600 ppm  $\text{NH}_3$ , 10%  $\text{O}_2$  in  $\text{N}_2$ , at a flow rate of 300 NmL/min. A Gasmet CX4000 Fourier transform infrared (FTIR) spectrometer is used to monitor the gas composition of the reactor exit gas and the feed gas by bypassing the reactor. Prior to the measurement, the sample is heated to 550  $^\circ\text{C}$ , in 10%  $\text{O}_2$  in  $\text{N}_2$  for 30 min, after which the feed gas is admitted to the reactor. The catalyst is then cooled down stepwise to 150  $^\circ\text{C}$ , and for each data point, the temperature is kept constant for 30 min.

## RESULTS

**Catalytic Cycles and Elementary Reactions.** The microkinetic models are based on the catalytic cycles for  $\text{NH}_3$ -SCR of NO to  $\text{N}_2$  and  $\text{H}_2\text{O}$  together with  $\text{N}_2\text{O}$  formation shown in Figures 2–4. The cycles are further developments (marked by red arrows in Figures 2 and 3) of the multisite reaction mechanism suggested in ref 18. The mechanisms consist of two reaction cycles that combine the formation of HONO and  $\text{H}_2\text{NNO}$  intermediates at the Cu sites with the decomposition of these intermediates to  $\text{N}_2$  and  $\text{H}_2\text{O}$  over Brønsted acid sites. A common step for both cycles is  $\text{O}_2$  adsorption on a pair of  $[\text{Cu}(\text{NH}_3)_2]^+$  complexes. A necessary condition to adsorb  $\text{O}_2$  is to have two  $[\text{Cu}(\text{NH}_3)_2]^+$  complexes located in the same zeolite

cage. The diffusion barrier of the complexes in CHA is small,<sup>17,51</sup> and the probability of having two complexes in the same cage is determined by the relative stability of paired and separated complexes. Based on the literature,<sup>17,52</sup> we estimate the relative stability of having two complexes in the same cage to be 0.3 eV lower than having complexes in different cages. The relative stability depends on the aluminum distribution together with how far the complexes are from the original Al site and could vary by some 0.1 eV. The chosen relative stability corresponds to a probability of  $6 \times 10^{-4}$  having two complexes in the same cage. Assuming two complexes in the same cage, the reaction cycle starts with the  $\text{O}_2$  adsorption step (reactions r1 and r17), when a  $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$  complex is formed, denoted by  $*-\text{OO}-*$ , where  $*$  represents  $[\text{Cu}(\text{NH}_3)_2]^+$ . The adsorption of  $\text{O}_2$  has a low energy barrier of 0.13 eV and is calculated to be exothermic by 0.20 eV. The two cycles follow different paths after the  $\text{O}_2$  adsorption.

In cycle I (Figure 2), NO adsorbs on a Cu cation (reaction r2) forming  $\text{NO}-\text{OO}-*$ . An additional  $\text{NH}_3$  molecule coordinates to  $\text{NO}-\text{OO}-*$  (reaction r3) and reacts (reaction r4) forming  $\text{H}_2\text{NNO}-\text{OOH}-*$ .  $\text{H}_2\text{NNO}$  desorbs from the Cu site (reaction r5) and diffuses to a Brønsted acid site (denoted by S). The reaction proceeds by subsequent NO and  $\text{NH}_3$  adsorption and the formation of  $\text{H}_2\text{NNO}-\text{OH}-\text{OH}$ . The second  $\text{H}_2\text{NNO}$  desorbs from the Cu site and diffuses to the Brønsted acid site (reaction r7), which allows adsorption of the third NO in the



**Figure 4.** Proposed reaction path for HONO and H<sub>2</sub>NNO decomposition over Brønsted acid sites.

reaction cycle (reaction r8) forming HONO–OH–\*. HONO desorbs (reaction r9) and reacts further over a Brønsted acid site. Once HONO desorbs, the remaining \*–OH–\* can react with NO to produce a second HONO (reactions r10 and r11). One alternative reaction path is adsorption of an additional NH<sub>3</sub>, forming NH<sub>3</sub>–OH–\* and \* (reaction r12). NO can adsorb on NH<sub>3</sub>–OH–\*, forming HONO (reaction r13), which desorbs and diffuses to a Brønsted acid site in reaction r14. In reaction r14, the additional NH<sub>3</sub> desorbs and the second linear [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complex is restored.

The presence of \*–OO–\* is crucial as it allows for NO adsorption. However, NH<sub>3</sub> can also adsorb on \*–OO–\*, which was not considered in ref 18. Possible structures for NH<sub>3</sub> adsorption onto \*–OO–\* are shown in Figure 1b,c. The adsorption energy of NH<sub>3</sub> is in structure (b) –0.98 eV, which is larger than the adsorption energy for NO, being –0.70 eV. An alternative structure is shown in Figure 1c, where the two Cu complexes are separated and O<sub>2</sub> is bound to only one Cu atom. In this case, the adsorption energy is –0.94 eV. Structures (b) and (c) are separated by a barrier of 0.33 eV. The possibility for NH<sub>3</sub> to adsorb on the \*–OO–\* complex has recently been observed experimentally with X-ray absorption spectroscopy, which was assigned to be a structure similar to (c).<sup>22</sup> We include (b) in the reaction cycle (reaction r15) as a lumped configuration describing both (b) and (c). After the adsorption of the additional NH<sub>3</sub> on \*–OO–\*, NO cannot adsorb on that complex, which implies that NH<sub>3</sub> adsorption blocks the site for further reactions.

In our recent work, we proposed a possible path for N<sub>2</sub>O formation within cycle I.<sup>12</sup> N<sub>2</sub>O may form as a side reaction by direct decomposition of H<sub>2</sub>NNO over H<sub>2</sub>NNO–OOH–\*. Once H<sub>2</sub>NNO–OOH–\* is formed after reaction r4, it is possible for H<sub>2</sub>NNO to transfer two H atoms to the OOH–\* intermediate (reaction r16) rather than to diffuse to the Brønsted acid sites (reaction r5). The decomposition of H<sub>2</sub>NNO into N<sub>2</sub>O and H<sub>2</sub>O is associated with a barrier of 0.40 eV (see Figure S3 in the Supporting Information).

Turning to cycle II (Figure 3), each O site of \*–OO–\* will adsorb one NO forming –ONOONO– (reactions r18 and r19). The complex separates into two ONO– (reaction r20) describing adsorbed nitrites (NO<sub>2</sub><sup>–</sup>). The separated complexes react subsequently with NO (reaction r21) and NH<sub>3</sub> (reaction r22) forming HONO–H<sub>2</sub>NNO (reaction r23). HONO and H<sub>2</sub>NNO desorb (reactions r24 and r25) and decompose into N<sub>2</sub>

and H<sub>2</sub>O at the Brønsted acid sites. At this point, the Cu sites are restored as linear complexes \*. Similar to cycle I, NH<sub>3</sub> may adsorb on \*–OO–\* (reaction r26) and hinder NO adsorption. We do not consider N<sub>2</sub>O formation in cycle II as H<sub>2</sub>NNO cannot decompose by hydrogen transfers in this cycle.

The H<sub>2</sub>NNO and HONO species that are generated over the Cu complexes in cycles I and II diffuse to the Brønsted acid sites and decompose into N<sub>2</sub> and H<sub>2</sub>O. The paths for HONO and H<sub>2</sub>NNO decomposition are shown in Figure 4, where S denotes a Brønsted acid site. Because NH<sub>3</sub> is strongly adsorbed on the Brønsted acid sites, the decomposition of H<sub>2</sub>NNO and HONO occurs over NH<sub>4</sub><sup>+</sup>. The HONO species reacts with an additional NH<sub>3</sub> (reaction r27) forming H<sub>2</sub>O and H<sub>2</sub>NNO–S, which together with H<sub>2</sub>NNO from the Cu site can decompose into N<sub>2</sub> and H<sub>2</sub>O (reaction r28). The mechanisms of H<sub>2</sub>NNO and HONO decomposition over Brønsted acid site have previously been discussed by us<sup>18</sup> and are similar to those reported by Li et al.<sup>53</sup>

It is important to note that the reaction cycles contain four types of NH<sub>3</sub>, with different roles in the low-temperature NH<sub>3</sub>-SCR reaction:

1. Ligand-NH<sub>3</sub>: NH<sub>3</sub> that adsorbs on the Cu cations, forming mobile [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes, which enable facile formation of pairs for O<sub>2</sub> adsorption. The ligand-NH<sub>3</sub> does not participate in the low-temperature SCR reaction provided that NH<sub>3</sub> is in excess.
2. Inhibiting NH<sub>3</sub>: NH<sub>3</sub> that adsorbs strongly on the [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> species, and thereby blocks the adsorption of NO, which is required for NH<sub>3</sub> SCR reaction.
3. Reactant-NH<sub>3</sub>: NH<sub>3</sub> that takes part in the reaction by reacting with NO.
4. NH<sub>4</sub><sup>+</sup>: NH<sub>3</sub> that is adsorbed at the Brønsted acid sites forming NH<sub>4</sub><sup>+</sup>.

This means that, in low-temperature NH<sub>3</sub>-SCR, NH<sub>3</sub> acts simultaneously as reactant, spectator, and inhibitor.

**Kinetics for NH<sub>3</sub>-SCR and N<sub>2</sub>O Formation.** The atomistic reaction cycles form the basis of the microkinetic model. The elementary reactions included in the microkinetic models together with the corresponding enthalpy and entropy barriers are given in Table 1. The corresponding electronic energy landscapes are shown in Figures S1 and S2 in the Supporting Information. The enthalpies for the main SCR cycles and the N<sub>2</sub>O formation are taken from refs 12 and 18, respectively. The

Table 1. Energy ( $\Delta E^\ddagger$ ) and Entropy ( $\Delta S^\ddagger$ ) Contributions to the Reaction Barriers of the Considered Elementary Steps<sup>a</sup>

no.	elementary step	$\Delta E^\ddagger$	$\Delta E^\ddagger_b$	$\Delta S^\ddagger$	$\Delta S^\ddagger_b$
Cu—Cycle I					
	$O_2 + 2^* \xrightarrow{r_1} ^*-OO-^*$	0.13	0.33	−134.9	17.6
r1	$O_2 + 2^* \xrightarrow{r_1} ^*-OO-^*$ (exp. $\Delta E$ ) (r1)	0.13	0.95	−134.9	17.6
r2	$NO + ^*-OO-^* \xrightarrow{r_2} NO-OO-^*$ (r2)	0.00	0.70	−109.2	0.0
r3	$NH_3 + NO-OO-^* \xrightarrow{r_3} NH_3NO-OO-^*$ (r3)	0.00	0.31	−65.6	0.0
r4	$NH_3NO-OO-^* \xrightarrow{r_4} H_2NNO-OOH-^*$ (r4)	0.05	0.54	−2.5	−44.4
r5	$H_2NNO-OOH-^* + S \xrightarrow{r_5} H_2NNO-S + ^*-OHO-^*$ (r5)	0.30	0.60	0.0	0.0
r6	$NO + NH_3 + ^*-OHO-^* \xrightarrow{r_6} H_2NNO-OH-OH$ (r6)	0.16	0.60	−3.2	38.8
r7	$H_2NNO-OH-OH + S \xrightarrow{r_7} H_2NNO-S + ^*-OHOH-^*$ (r7)	0.30	0.60	0.0	0.0
r8	$NO + ^*-OHOH-^* \xrightarrow{r_8} HONO-OH-^*$ (r8)	0.10	0.39	−120.9	0.0
r9	$HONO-OH-^* + S \xrightarrow{r_9} HONO-S + ^*-OH-^*$ (r9)	0.30	0.60	0.0	0.0
r10	$NO + ^*-OH-^* \xrightarrow{r_{10}} [HONO-^* + ^*]$ (r10)	0.10	1.03	−120.9	0.0
r11	$[HONO-^* + ^*] + S \xrightarrow{r_{11}} HONO-S + 2^*$ (r11)	0.30	0.60	0.0	0.0
r12	$NH_3 + ^*-OH-^* \xrightarrow{r_{12}} [NH_3-OH-^* + ^*]$ (r12)	0.00	0.97	−90.4	0.0
r13	$NO + [NH_3-OH-^* + ^*] \xrightarrow{r_{13}} [HONO-NH_3-^* + ^*]$ (r13)	0.00	0.32	−120.9	0.0
r14	$[HONO-NH_3-^* + ^*] + S \xrightarrow{r_{14}} NH_3 + HONO-S + 2^*$ (r14)	0.30	0.60	90.4	0.0
r15	$NH_3 + ^*-OO-^* \xrightarrow{r_{15}} NH_3-OO-^*$ (r15)	0.00	0.98	−103.8	0.0
r16	$H_2NNO-OOH-^* \xrightarrow{r_{16}} N_2O + H_2O + ^*-OH-^*$ (r16)	0.40	2.61	2.7	−301.4
Cu—Cycle II					
r17	$O_2 + 2^* \xrightarrow{r_{17}} ^*-OO-^*$ (exp. $\Delta E$ ) (r17)	0.13	0.95	−134.9	17.6
r18	$NO + ^*-OO-^* \xrightarrow{r_{18}} -ONOO-^*$ (r18)	0.00	1.65	−143.4	0.0
r19	$NO + -ONOO-^* \xrightarrow{r_{19}} -ONOONO-$ (r19)	0.00	1.65	−143.4	0.0
r20	$-ONOONO- \xrightarrow{r_{20}} 2ONO-$ (r20)	0.37	0.40	−41.5	−7.4
r21	$NO + ONO- \xrightarrow{r_{21}} ONO-NO$ (r21)	0.00	0.91	−132.3	0.0
r22	$NH_3 + ONO-NO \xrightarrow{r_{22}} ONO-NONH_3$ (r22)	0.00	0.67	−65.6	0.0
r23	$ONO-NONH_3 \xrightarrow{r_{23}} HONO-H_2NNO$ (r23)	0.62	0.80	−14.6	12.5
r24	$HONO-H_2NNO + S \xrightarrow{r_{24}} H_2NNO-^* + HONO-S$ (r24)	0.30	0.60	0.0	0.0
r25	$H_2NNO-^* + S \xrightarrow{r_{25}} H_2NNO-S + ^*$ (r25)	0.30	0.60	0.0	0.0
r26	$NH_3 + ^*-OO-^* \xrightarrow{r_{26}} NH_3-OO-^*$ (r26)	0.00	0.98	−103.8	0.0
Bronsted Acid Site					
r27	$NH_3 + HONO-S \xrightarrow{r_{27}} H_2NNO-S + H_2O$ (r27)	0.38	0.93	19.7	−194.6
r28	$H_2NNO-S \xrightarrow{r_{28}} H_2O + N_2 + S$ (r28)	0.38	2.08	−70.1	−294.4

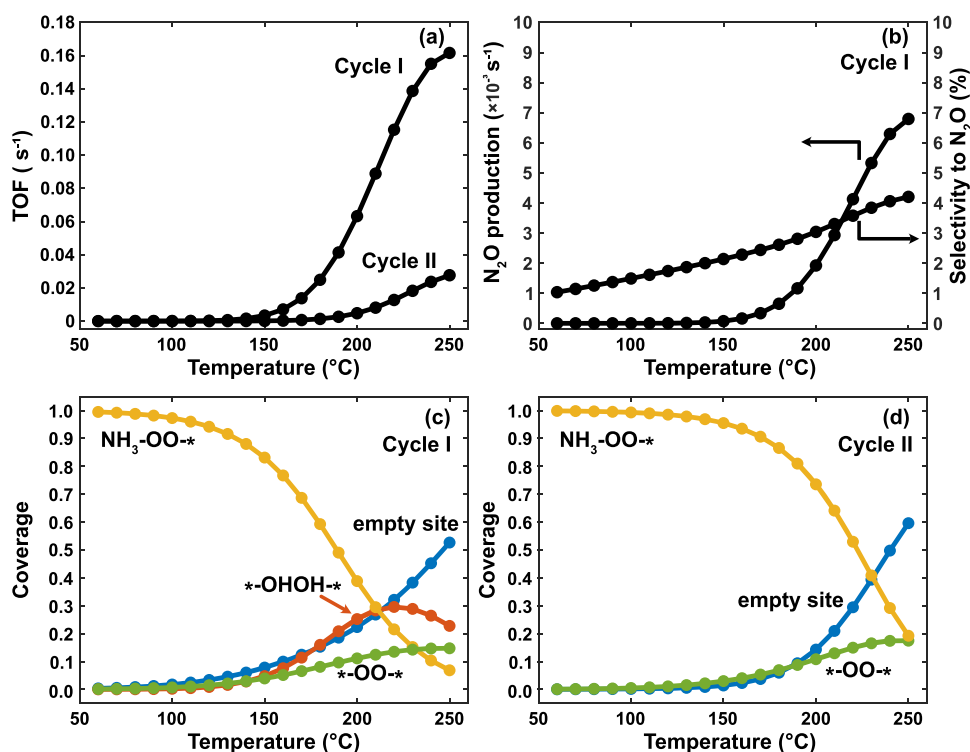
<sup>a</sup>Reaction r20 involves the separation of the paired linear complexes, resulting in the stoichiometric 2 on the product side. Reactions r21–r25 are in the simulations doubled to account for two parallel reactions on separated complexes. Energy is given in eV and entropy in J/(mol·K). The \* and S in the elementary steps represent one  $[Cu(NH_3)_2]^+$  complex and one  $NH_4^+$ , respectively.

two cycles are decoupled in the simulations. The enthalpy barriers including zero-point corrections are evaluated using DFT as discussed above with the exception of  $O_2$  adsorption. In the kinetic simulations, the adsorption energy of  $O_2$  has been adjusted to the recently reported experimental value of 0.82 eV.<sup>24</sup> The difference between the experimental and calculated values can be traced to the arbitrariness in the choice of the initial state structure for the two  $[Cu(NH_3)_2]^+$  complexes<sup>24</sup> and the issue describing molecular oxygen with the applied exchange–correlation functional.<sup>38</sup> In addition, the barriers for

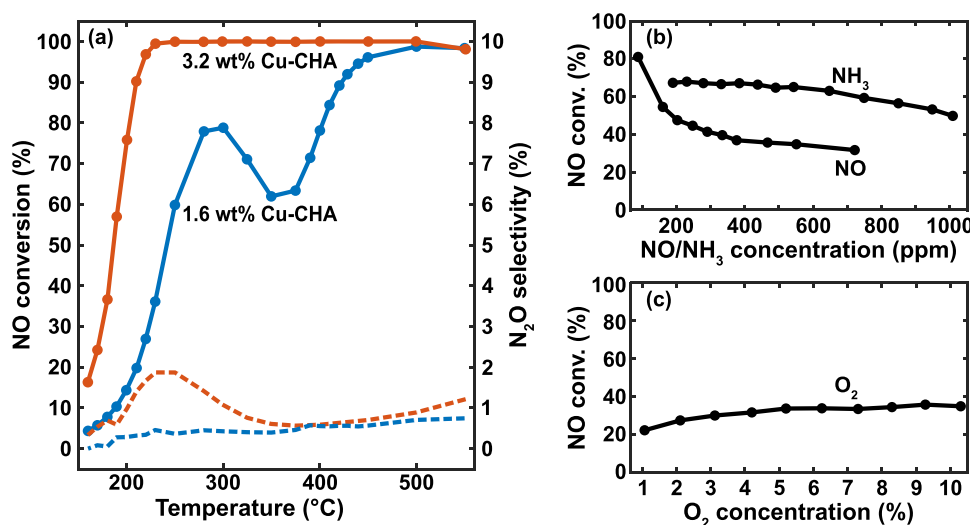
reactions r8 and r10 are set to 0.10 eV instead of the computed zero barriers to avoid numerical instabilities.

The highest energy barriers ( $\Delta E^\ddagger$ ) in cycle I for  $NH_3$ -SCR are the decomposition of HONO and  $H_2NNO$  ( $\sim 0.4$  eV), which is similar to the barrier for  $N_2O$  formation. The highest barrier in cycle II is instead the formation of  $H_2NNO$ , which has a barrier of 0.62 eV. The barriers for HONO and  $H_2NNO$  diffusion (0.30 eV) are based on molecular dynamics simulations, which include both desorption from the Cu sites and passage through the eight-membered zeolite rings.





**Figure 5.** (a) Simulated turnover frequency for NO conversion over Cu-CHA as a function of temperature in cycles I and II. (b) N<sub>2</sub>O formation and selectivity over Cu-CHA in cycle I. (c, d) Coverage of dominating states in cycles I and II. The fractional coverage should in this case be understood as the fraction of Cu sites being in a certain state of the reaction cycle. The simulations are performed with 600 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, and balance N<sub>2</sub>.



**Figure 6.** (a) NO conversion (solid lines) and N<sub>2</sub>O formation (dashed lines) versus temperature for standard NH<sub>3</sub>-SCR over the 1.6 wt % Cu-CHA (blue) and 3.2 wt % Cu-CHA (red) samples. Feed: 500 ppm NO, 600 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, and balance N<sub>2</sub>. The conversion at 200 °C for the 1.6 wt % Cu-CHA sample corresponds to an apparent reaction rate of 0.02 mol NO/(mol Cu·s). (b, c) NO conversion over the 1.6 wt % Cu-CHA sample versus the concentration of NO, NH<sub>3</sub>, and O<sub>2</sub> at 200 °C. In this series of experiments, individual feed gas concentrations are changed when all other feed gases concentrations are held constant. NH<sub>3</sub> concentration is fixed at 843 ppm when the NO concentration is varied. The NO concentration is set to 139 ppm when the NH<sub>3</sub> concentration is varied. When the concentrations of O<sub>2</sub> are changed from 1 to 10%, the concentrations of NH<sub>3</sub> and NO are set to 641 and 381 ppm, respectively. The balancing gas in the reaction order experiments is Ar.

As we consider the reaction over [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes, the cycles describe standard NH<sub>3</sub>-SCR in the low-temperature regime (below ~250 °C), where the decomposition of the [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complex is negligible.<sup>54</sup> The model does not describe the reaction above ~250 °C, where the contribution of framework-bound Cu becomes important.<sup>54</sup> The simulations

are performed for a total pressure of 1 atm, with 600 ppm NH<sub>3</sub>, 500 ppm NO, 10% of O<sub>2</sub>, and balance N<sub>2</sub>. In the absence of reactants, the ratio between pairs of [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> complexes and the Brønsted acid sites is set to 1.

**Turnover Frequency (TOF) and Coverages.** The calculated turnover frequencies (TOFs) of cycles I and II are presented in

**Figure 5a.** The TOFs in both cycles have well-defined onset temperatures of about 120 and 170 °C in cycles I and II, respectively. The TOF of cycle I is significantly higher than that of cycle II. In both cases, the TOF begins to decrease at temperatures above ~235 °C. The decrease in TOF is due to low surface coverages as the decomposition of the  $[\text{Cu}(\text{NH}_3)_2]^+$  complexes is not included in our model. The TOF is calculated as the number of consumed NO per Cu complex accounting for the probability of having two Cu complexes in the same CHA cage.

By comparing the turnover frequency and the coverages of the most abundant species reported in **Figure 5c,d**, it is clear that  $\text{NH}_3$  adsorption inhibits the  $\text{NH}_3$ -SCR reaction in the low-temperature regime (<120 °C). The coverage of inhibiting  $\text{NH}_3$  (denoted by  $\text{NH}_3\text{-OO-}^*$ ) is close to 1 below 100 °C for cycle I, whereas this regime extends to 150 °C for cycle II. The inhibiting  $\text{NH}_3$  desorbs as the temperature is increased, allowing for the adsorption of NO and the formation of  $\text{H}_2\text{NNO}$  and HONO. The TOF increases with increasing  $^*\text{-OHOH-}^*$  coverage, which peaks at 230 °C. The number of empty sites increases and begins to dominate above 230 °C, yielding a decrease in the TOF at high temperatures. The analysis of the coverages shows that the reaction at low temperatures is determined by the adsorption energy of the  $\text{NH}_3$  that blocks the  $^*\text{-OO-}^*$  sites. A weaker bond strength of  $\text{NH}_3\text{-OO-}^*$  would facilitate the reaction at lower temperatures.

**Figure 5b** shows the TOF and the corresponding selectivity for  $\text{N}_2\text{O}$  formation in cycle I. The temperature dependence of  $\text{N}_2\text{O}$  formation is similar to that of  $\text{NH}_3$ -SCR with a peak at 230 °C. This is in agreement with experimental reports<sup>55,56</sup> and a consequence of  $\text{N}_2\text{O}$  formation over Cu sites via  $\text{H}_2\text{NNO}$ . The selectivity to  $\text{N}_2\text{O}$  increases from 2 to 4% in the temperature interval of 150 to 250 °C.

The  $\text{NH}_3$ -SCR reaction is a multisite reaction requiring both Cu and Brønsted acid sites, whereas  $\text{N}_2\text{O}$  formation only requires the Cu sites. This difference means that the  $\text{NH}_3$ -SCR reaction depends on both the Cu loading and the Cu/Al ratio, whereas  $\text{N}_2\text{O}$  formation depends primarily on the Cu loading. This implies that the selectivity for  $\text{N}_2$  formation can be increased by decreasing the Cu/Al ratio. In this case, **reaction r5** is favored over **reaction r16** as the ratio of Brønsted acid sites is increased with respect to Cu sites.

**Comparison to Experimental Data.** To verify the microkinetic model, we compare the results with a set of kinetic experiments. **Figure 6a** shows the temperature dependence of NO conversion and  $\text{N}_2\text{O}$  selectivity for the 1.6 wt % Cu-CHA and 3.2 wt % Cu-CHA samples under standard SCR conditions. The conversion profile for the 1.6 wt % Cu-CHA catalyst shows the characteristic bimodal shape with a local maximum at about 275 °C. The onset temperature for the conversion of NO decreases with increasing Cu loading. The apparent activation energies (**Table 2**) derived from the  $\text{NO}_x$  conversion experiments in the 160–240 °C range are 0.62 and 0.89 eV for the 1.6 wt % Cu-CHA and 3.2 wt % Cu-CHA catalysts, respectively. The calculated apparent activation energies from the first-principles microkinetic model are 0.75 eV for cycle I including  $\text{NH}_3$  inhibition, 0.31 eV without  $\text{NH}_3$  inhibition (**reaction r15**), and 1.06 eV for cycle II with inhibition. The higher activity together with an apparent activation energy matching the experiments points to cycle I as the main reaction path for  $\text{NH}_3$ -SCR. Furthermore, the results show that the apparent activation energy for  $\text{NH}_3$ -SCR mainly is determined by the  $\text{NH}_3$  inhibition of the  $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$  complex. The preference

**Table 2.** Apparent Activation Energy ( $E_{\text{app}}$ ) and Reaction Orders ( $n_x$ ) from Experiments and the Kinetic Models<sup>a</sup>

	exp.	cycle I	cycle I (without reaction r15)	cycle II	cycle II (without reaction r26)
$E_{\text{app}}$	0.62/0.89	0.75	0.31	1.06	0.05
$n_{\text{NH}_3}$	−0.23	−0.22	0.05	−0.76	0.00
$n_{\text{NO}}$	0.73	0.95	0.92	1.00	0.99
$n_{\text{O}_2}$	0.25	0.23	0.34	0.15	0.58

<sup>a</sup>The simulated reaction orders are evaluated at 200 °C. The energy is given in electronvolt.

of cycle I is supported by the thermodynamic preference for **reaction r2** compared to **reaction r18**. The probability of following cycle I is about 98 % in the considered temperature regime.

The selectivity for  $\text{N}_2\text{O}$  is calculated for cycle I. To explore the dependence of the selectivity on the Cu/Al ratio, we model the formation of  $\text{N}_2\text{O}$  with different Cu/Al ratios by changing the ratio between  $[\text{Cu}(\text{NH}_3)_2]^+$  and Brønsted acid sites in the model. Reducing the Cu/Al ratio to 0.33 decreases the selectivity to  $\text{N}_2\text{O}$  by a factor of 2 (see **Figure S6** in the Supporting Information). The simulations match the experimental observation that  $\text{N}_2\text{O}$  formation for the 3.2 wt % Cu-CHA catalyst (Cu/Al ratio of 0.24) is significantly higher than that for the 1.6 wt % Cu-CHA catalyst (Cu/Al ratio of 0.12).

The microkinetic model also predicts reaction orders with respect to  $\text{NH}_3$ , NO, and  $\text{O}_2$  in good agreement with experiments. **Figure 6b,c** shows the measured dependence of the  $\text{NO}_x$  conversion with changes in the partial pressures of  $\text{NH}_3$ , NO, and  $\text{O}_2$  for the 1.6 wt % Cu-CHA catalyst. The reaction orders for  $\text{NH}_3$ -SCR derived from these data are −0.23 for  $\text{NH}_3$ , 0.73 for NO, and 0.25 for  $\text{O}_2$ , which are in accordance with previous measurements.<sup>4,7,19,57</sup> The values for NO and  $\text{O}_2$  agree very well with the calculated values of cycle I that includes the  $\text{NH}_3$  inhibition (−0.22 for  $\text{NH}_3$ , and 0.23 for  $\text{O}_2$ ), whereas the calculated reaction order for NO (0.95) is slightly higher than the measured value. The reaction order in  $\text{O}_2$  has been measured to decrease with increasing  $\text{O}_2$  pressure and increasing Cu/Al ratio.<sup>57</sup> The model reproduces these trends as shown in the **Supporting Information (Table S1)**. The model also predicts the experimental increase in TOF as a function of  $\text{O}_2$  pressure (**Figure S7**). The reaction orders for cycle II are not in such good agreement with experiments, again indicating that cycle I is the main reaction path for  $\text{NH}_3$ -SCR.

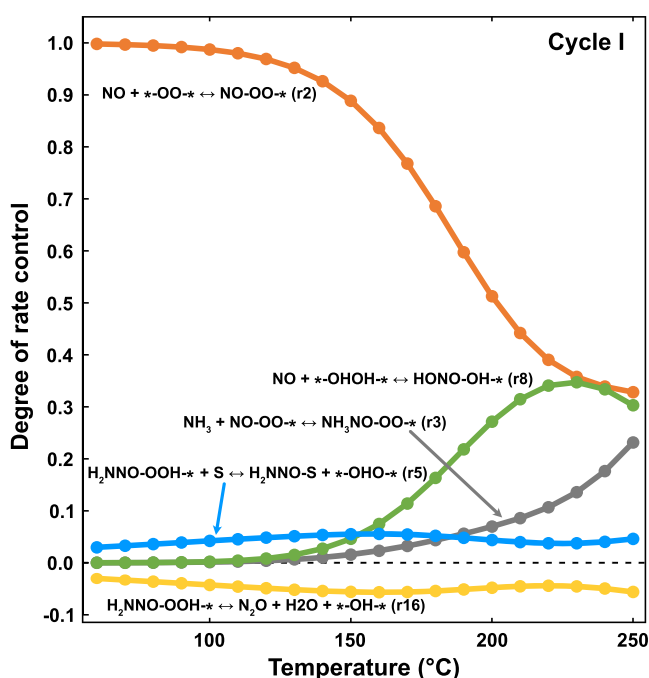
The reaction orders analysis further exemplifies that  $\text{NH}_3$  inhibition plays an important role in the kinetics of the  $\text{NH}_3$ -SCR reaction. The negative reaction order with respect to  $\text{NH}_3$  is a direct consequence of the  $\text{NH}_3$  inhibition as clearly shown by the calculated reaction order of +0.05 when omitting the  $\text{NH}_3$  inhibition. Furthermore, the calculated apparent activation energy for cycle I becomes much lower, when the  $\text{NH}_3$  inhibition is omitted, showing that the apparent activation energy is determined by the desorption of inhibiting  $\text{NH}_3$ . This indicates that the  $\text{NH}_3$  inhibition is a crucial reaction that should be included in kinetic models for  $\text{NH}_3$ -SCR over Cu-CHA at low temperatures.

The discrepancy between the calculated and measured reaction order with respect to NO is probably due to effects of residual water and parallel reactions on minority Cu sites, such as framework-bound Cu, which could affect the reaction order.

**Degree of Rate Control Analysis for NH<sub>3</sub>-SCR.** The comparison to experiments shows that the first-principles microkinetic model captures the measured kinetic behavior. It motivates a further elaboration of which elementary steps that control the reaction by performing a degree of rate control ( $\chi_i$ ) analysis.<sup>58</sup> This analysis is performed by increasing the value of rate constants for the forward and backward reactions for each elementary step by 1% while keeping the equilibrium constant and the rate constants of all other reaction steps fixed. By calculating the response in the total TOF, the role of each elementary reaction is monitored.  $\chi_i$  is calculated according to

$$\chi_i = \frac{k_i}{r} \left( \frac{\partial \text{TOF}}{\partial k_i} \right)_{K_i} \quad (9)$$

The result of the degree of rate control analysis for NH<sub>3</sub>-SCR in cycle I is shown in Figure 7. We focus on cycle I, as this cycle



**Figure 7.** Degree of rate control analysis for NH<sub>3</sub>-SCR over Cu-CHA in cycle I. The simulation is performed with 600 ppm NH<sub>3</sub>, 500 ppm NO, 10% O<sub>2</sub>, and balance N<sub>2</sub>.

dominates the TOF and reproduces the measured reaction orders and apparent activation energy. Only the reactions with a notable degree of rate control are shown in Figure 7. The sum of all degrees of rate control is 1.

At low temperatures, the rate of NH<sub>3</sub>-SCR is mainly determined by the NO adsorption step (reaction r2), as a consequence of the strong inhibition effect of NH<sub>3</sub>. As the temperature increases to 230 °C, the controlling effect of NO adsorption is gradually reduced, whereas the formation of HONO-OH-\* (reaction r8) becomes increasingly important. NO adsorption and HONO-OH-\* formation reach an equal degree of rate control at 230 °C, which is the temperature for the maximum TOF. The analysis shows that the N<sub>2</sub>O formation (reaction r16) is a competing reaction with a negative degree of rate control. The diffusion of H<sub>2</sub>NNO (reaction r5) from the Cu site to the Brønsted acid site has an opposite degree of rate

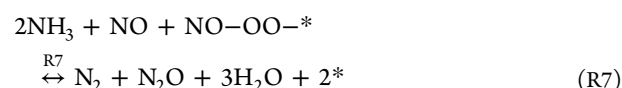
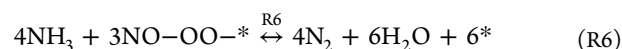
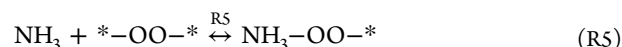
control compared to reaction r16, which signals the branching in the reaction cycle.

## DISCUSSION AND SIMPLIFIED MODEL

Having access to a first-principles microkinetic model makes it possible to link the kinetic behavior to certain reaction intermediates and structures in the Cu-CHA catalyst. The apparent activation energy is related to the desorption of the inhibiting NH<sub>3</sub>, which blocks the [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> sites for NO adsorption. This explains the sizable apparent activation energy despite the flat potential energy landscape. The NH<sub>3</sub> inhibition is also reflected in the negative reaction order with respect to NH<sub>3</sub>. The positive reaction order with respect to O<sub>2</sub> is a consequence of that O<sub>2</sub> adsorption is required for the NH<sub>3</sub>-SCR reaction over [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> pairs. The adsorption of O<sub>2</sub> changes the oxidation state from Cu<sup>I</sup> to Cu<sup>II</sup>, which allows for NO and NH<sub>3</sub> adsorption and the subsequent formation of H<sub>2</sub>NNO and HONO.

The alternation between Cu<sup>I</sup> and Cu<sup>II</sup> (and possibly Cu<sup>III</sup>) is central for the function of the Cu-CHA catalyst, and the temperature dependence of the Cu-oxidation state has been measured to characterize the catalyst during reaction conditions.<sup>19,56</sup> From an analysis of the Cu species present during the NH<sub>3</sub>-SCR reaction, we find that the fractions of Cu<sup>I</sup> and Cu<sup>II</sup> are around 50% in the considered temperature range (150–250 °C). The fraction of Cu<sup>II</sup> reaches a maximum of 57% at 210 °C and decreases to 42% at 250 °C (see Figure S9 in the Supporting Information). The calculated values match experimental reports on the basis of in situ X-ray absorption measurements.<sup>19</sup>

Although the microkinetic model gives a precise description of the NH<sub>3</sub>-SCR reaction, it is a complicated reaction network that contains 18 elementary steps. To connect to previous phenomenological models, we simplify the atomistic model to only five reactions where we describe the adsorption of O<sub>2</sub> over a pair of [Cu(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, the adsorption of NO and NH<sub>3</sub> on the [Cu<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>O<sub>2</sub>]<sup>2+</sup> complex as elementary steps and the formation of N<sub>2</sub> and H<sub>2</sub>O are lumped in two steps as follows



These reactions for low-temperature NH<sub>3</sub>-SCR and N<sub>2</sub>O formation (see the SI for parameters) describe the temperature dependence of the TOF with reasonable accuracy, having an apparent activation energy of 0.86 eV and reaction orders with respect to O<sub>2</sub>, NO, and NH<sub>3</sub> of 0.2, 1.2, and −0.3, respectively. We find it important to treat the adsorption of O<sub>2</sub>, NO, and NH<sub>3</sub> explicitly to obtain a qualitative agreement with the detailed model, which is consistent with the kinetic analysis showing that these adsorption steps control the reaction. Our simplified model can be compared to the phenomenological model in ref 14, where the lumped NH<sub>3</sub>-SCR reaction was reported to have an apparent activation energy of 0.71 eV. Our analysis shows



that the apparent activation energy is related to the desorption of  $\text{NH}_3$  from the  $[\text{Cu}_2(\text{NH}_3)_4\text{O}_2]^{2+}$  complex.

## CONCLUSIONS

We have developed a first-principles microkinetic model for low-temperature  $\text{NH}_3$ -SCR and  $\text{N}_2\text{O}$  formation over Cu-CHA catalysts, based on DFT calculations and detailed entropy analysis. The model includes  $\text{H}_2\text{NNO}$  and HONO formation over mobile Cu species together with  $\text{N}_2$  and  $\text{H}_2\text{O}$  formation over Brønsted acid sites.  $\text{N}_2\text{O}$  formation is included via  $\text{H}_2\text{NNO}$  decomposition over Cu sites. The calculated values for activation energy and reaction orders for NO,  $\text{NH}_3$ , and  $\text{O}_2$ , based on this microkinetic model, agree well with experimentally determined values. The favorable comparison between the model and the kinetic experiments strengthens the validity of the suggested multisite reaction mechanisms for low-temperature  $\text{NH}_3$ -SCR and  $\text{N}_2\text{O}$  formation over Cu-CHA.

The atomistic description allows for a clear link between kinetic behavior and materials properties. At low temperatures,  $\text{NH}_3$  inhibits the reaction by occupying Cu sites for NO adsorption. The  $\text{NH}_3$  inhibition is reduced with increasing temperature allowing for NO adsorption and subsequent formation of HONO and  $\text{H}_2\text{NNO}$ . The potential energy surface is flat, and the low-temperature apparent activation energy is determined by the adsorption energy of the inhibiting  $\text{NH}_3$ , which hinders the reaction at low temperatures.

We find that  $\text{N}_2\text{O}$  selectivity is moderately affected by the temperature. Thus,  $\text{N}_2\text{O}$  selectivity cannot be steered by controlling the operational temperature. However, as low-temperature  $\text{N}_2$  formation requires both Cu and Brønsted acid sites, whereas  $\text{N}_2\text{O}$  formation requires only Cu sites, Cu/Al ratio and Al distribution may provide handles to reduce  $\text{N}_2\text{O}$  emissions.

Our work demonstrates the capabilities of first-principles microkinetic models for reactions in zeolites with dynamic active sites. The developed model advances the conceptual understanding of low-temperature  $\text{NH}_3$ -SCR over Cu-CHA, rationalizes previous phenomenological models, and can be used to further enhance the performance of the catalyst.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c03973>.

Energy landscapes for cycles I and II,  $\text{H}_2\text{NNO}$  adsorption on the  $[\text{Cu}(\text{NH}_3)_4\text{OOH}]^{2+}$  complex, energy profile for  $\text{H}_2\text{NNO}$  diffusion, fit of entropy scaling factor by comparison with the  $\text{NH}_3$  temperature-programmed desorption (TPD) profiles, analysis of the effect of Cu/Al ratio on selectivity, dependence of  $\text{O}_2$  reaction order on oxygen pressure, temperature-dependent fractions of  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$ , parameters and results of the simplified kinetic model (PDF)

Atomic structure files (ZIP)

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### Notes

The authors declare no competing financial interest.

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